Supporting Information for

Significant Capacitance Enhancement via in situ Exfoliation of Quasi-One-Dimensional Graphene Nanostripes in Supercapacitor Electrodes

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Supplementary Note 1

Disordered carbon materials (including graphene, due to stacking disorder) typically do not demonstrate well defined lithium intercalation potentials.[1] For example, while galvanostatic lithiation and delithiation of crystalline graphite results in well-defined voltage plateaus (see Fig. 8 in references[1]), galvanostatic lithiation and delithiation of graphene electrodes results in a quasi-exponential curves rather than voltage plateaus as in references[2,3] and in Fig. S1a. The absence of voltage plateaus in these curves suggest that the lithium intercalation potentials are continuously distributed throughout the voltage range (even at voltages as high as 2~3 V vs Li/Li^+). To demonstrate the intercalation phenomenon at ~2.5 V more quantitatively, we performed higher resolution galvanostatic discharge/charge measurements at ~2.5 V. Fig. S1b (Fig. S1c) shows the first 5 seconds of a galvanostatic discharge (charge) curve after holding the voltage for 5 minutes. A purely capacitive process would result in a linear curve with some non-zero slope, while a purely faradaic process would result in a linear curve with zero slope (*i.e.*, a plateau).[4] In practice, however, every electrode forms electric double-layers, and electric double-layer processes are fast. Therefore, when currents are applied to an electrode, the initial response is typically a capacitive double-layer effect, followed by faradaic processes (if relevant).[4]

In the case of graphene, the intercalation potentials are not well defined so a voltage plateau is not observed even after the capacitive double-layer response. Instead, a gentle slope is observed after the capacitive double-layer response. This phenomenon is observed in Fig. S1b (Fig. S1c), where the slope is initially more negative (more positive). To emphasize this change in slope, we plotted the derivative of voltage with respect to time. The derivative curve clearly demonstrates an initial slope that is more negative (more positive) than the subsequent response, highlighting that two different processes are present. We suggest that the region of steeper slope is the capacitive double-layer response, and the region of more gentle slope involves intercalation. Additionally, the change in slope should not be interpreted as series resistance as series resistance is not time dependent.[4]

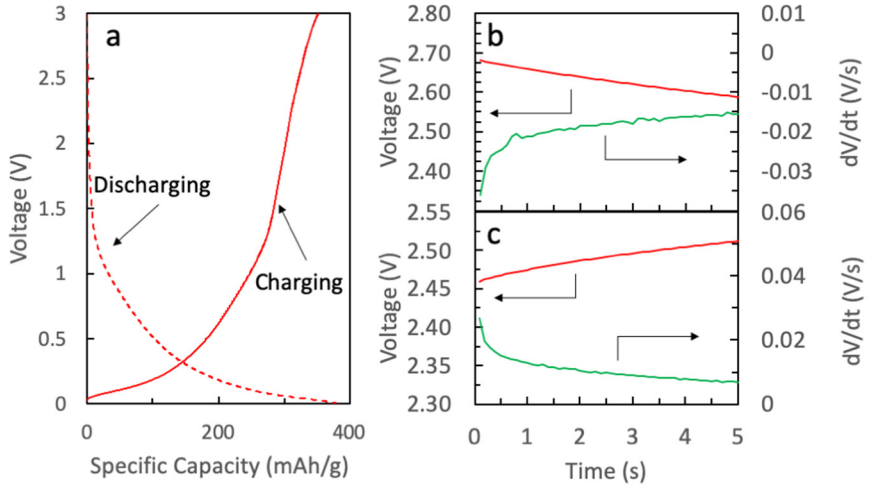

Figure S1. (a) Galvanostatic discharge and charge of fifth cycle of graphene electrode. First 5 seconds of galvanostatic discharge (b) and charge (c) and their derivatives. Current: 100 mA/g.

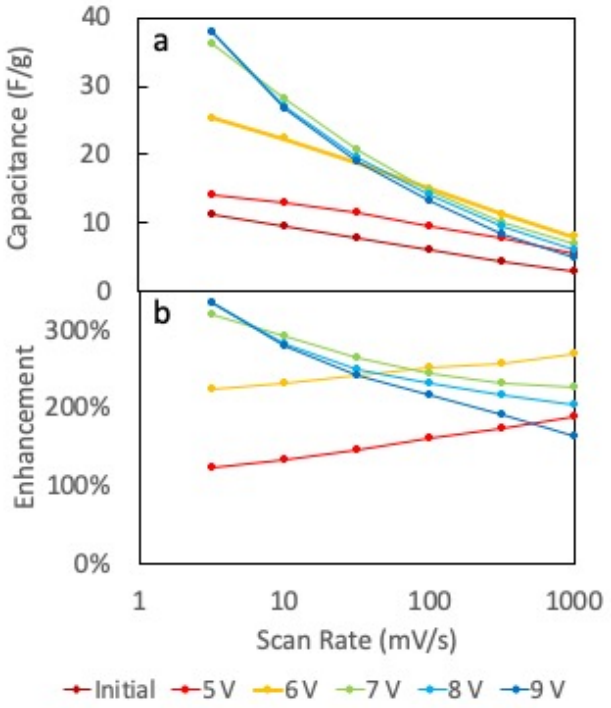

Figure S2. Capacitance (a) and enhancement (b) of graphene exfoliated *in situ* via high voltage exfoliation only.

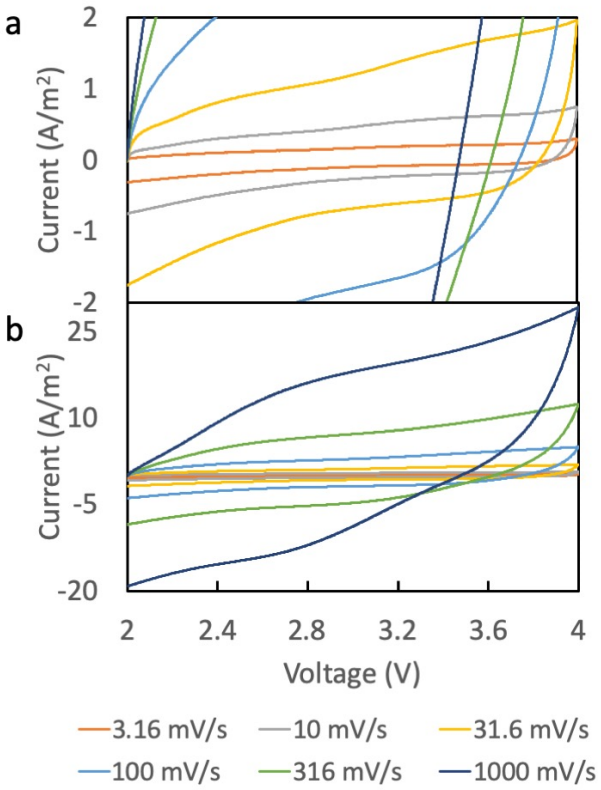

Figure S3. Reduced scale (a) and full scale (b) cyclic voltammetry curves of pre-exfoliated graphene supercapacitor electrode. Voltage is vs Li/Li^+.

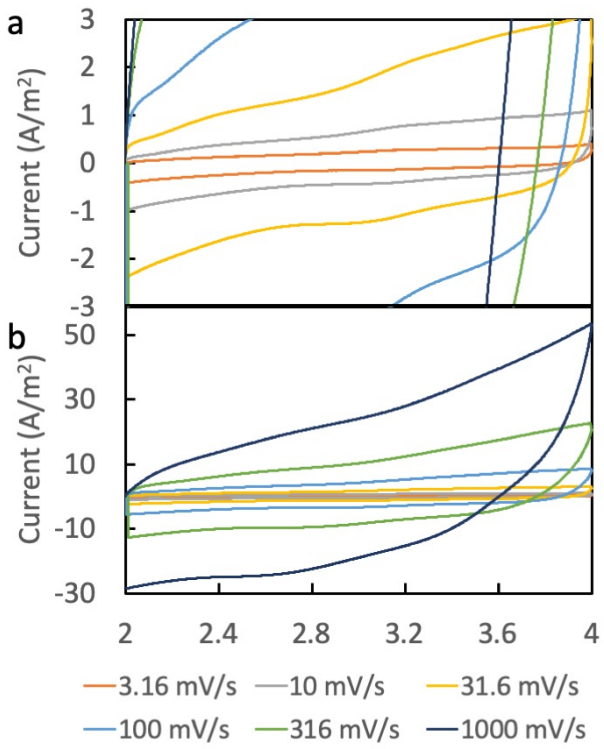

Figure S4. Reduced scale (a) and full scale (b) cyclic voltammetry curves of graphene supercapacitor electrode exfoliated at 5 V. Voltage is vs Li/Li^+.

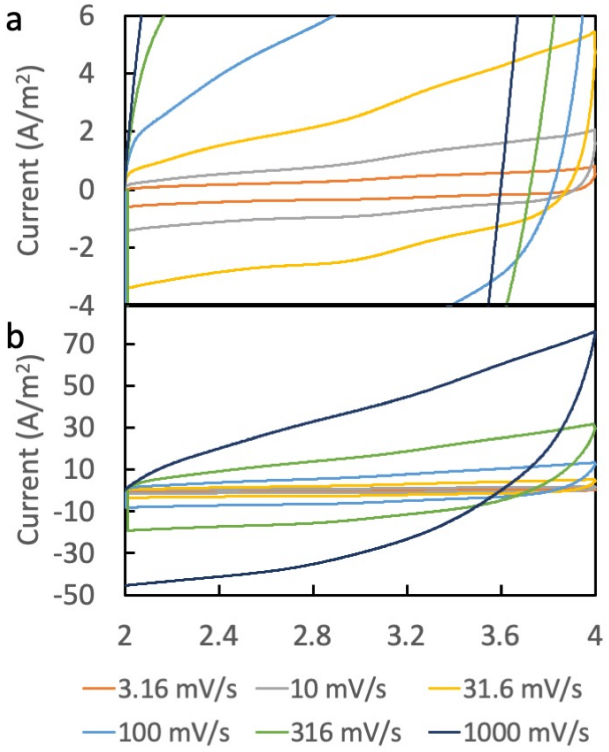

Figure S5. Reduced scale (a) and full scale (b) cyclic voltammetry curves of graphene supercapacitor electrode exfoliated at 6 V. Voltage is vs Li/Li^+.

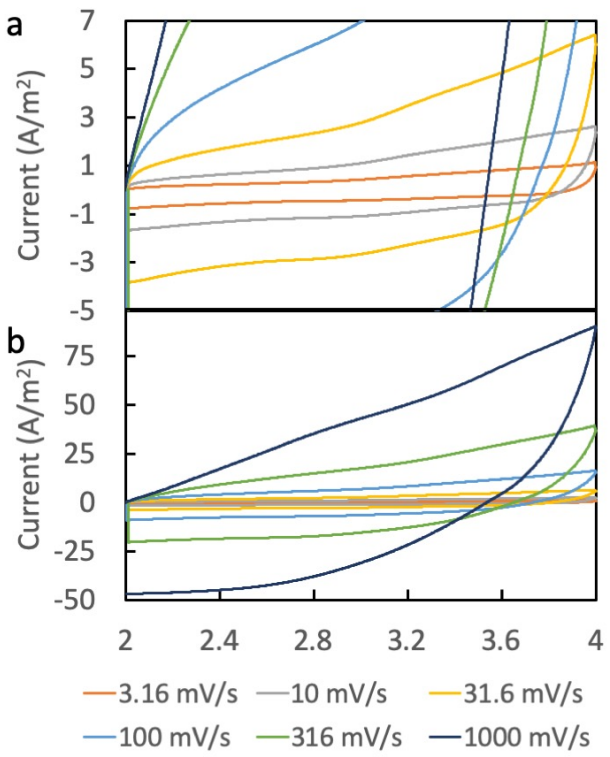

Figure S6. Reduced scale (a) and full scale (b) cyclic voltammetry curves of graphene supercapacitor electrode exfoliated at 7 V. Voltage is vs Li/Li^+.

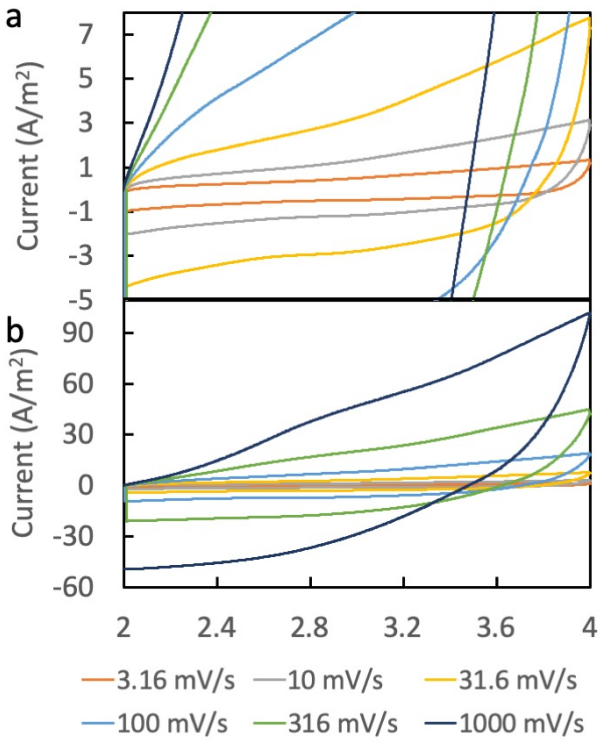

Figure S7. Reduced scale (a) and full scale (b) cyclic voltammetry curves of graphene supercapacitor electrode exfoliated at 8 V. Voltage is vs Li/Li^+.

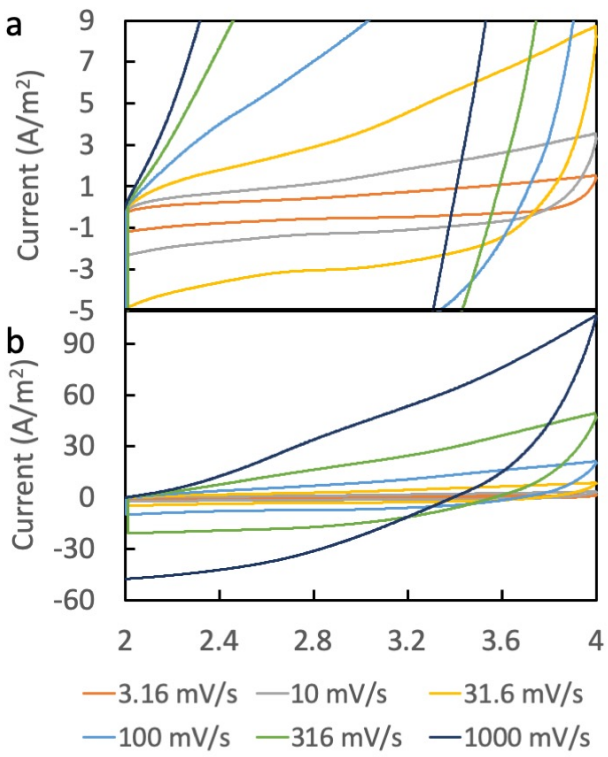

Figure S8. Reduced scale (a) and full scale (b) cyclic voltammetry curves of graphene supercapacitor electrode exfoliated at 9 V. Voltage is vs Li/Li^+.

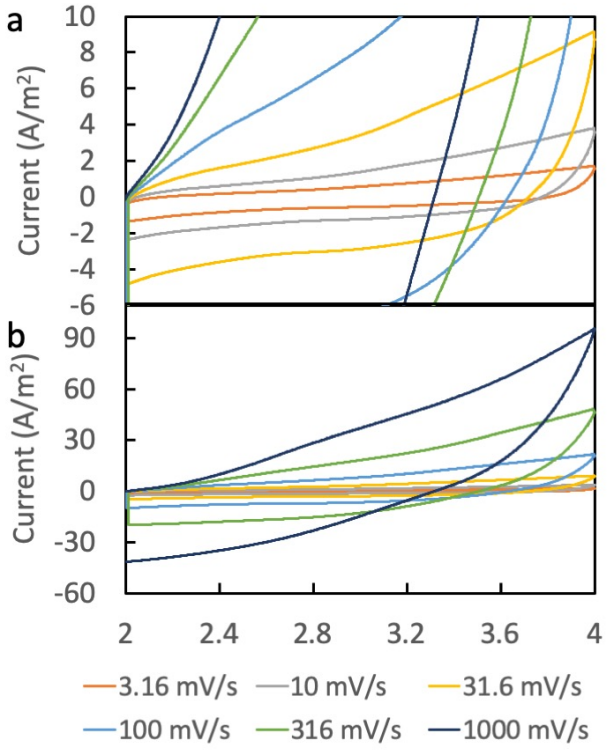

Figure S9. Reduced scale (a) and full scale (b) cyclic voltammetry curves of graphene supercapacitor electrode exfoliated at 10 V. Voltage is vs Li/Li^+.

Supplementary Note 2

Ideally, we could directly measure the surface area of exfoliated graphene materials (*e.g.*, via BET surface area measurement) to compare the result with that of the original material. However, typical surface area measurements (*e.g.*, BET surface area measurement) would require a fairly large amount of material (compared to typical electrode masses) and the removal of graphene material from the coin cell current collector (*e.g.*, by scrapping it off), which would likely affect the accurate determination of the surface area. Therefore, to substantiate the notion that the surface area increased with exfoliation, we extrapolated the double-layer capacitance (which is proportional to the surface area) from the cyclic voltammograms.

Strictly speaking, the double-layer capacitance may differ from the total capacitance because additional processes (*e.g.*, intercalation behavior as discussed previously) may take place during the total capacitance measurement. To ensure better determination of the double-layer capacitance, we employed a method discussed in Bard and Faulkner's *Electrochemical Methods*,[4] which relied on analyzing the initial current (i) response of a linear potential sweep. In the absence of faradaic processes, the initial current is described by

$$i = \nu C_d \left[1 - \exp\left(-\frac{t}{R_s C_d}\right)\right], \quad \text{(S1)}$$

where ν is the voltage scan rate, C_d is the double-layer capacitance, t is the time and R_s is the solution resistance.

The initial current response of each electrode for a scan rate of 3.16 mV/s is shown in Fig. S10a. The exponential component is visible in the initial current response, and with increasing exfoliation voltage the exponential component extends to longer times. To quantitatively understand the changes in the double-layer capacitance, we fit these curves to the following expression:

$$i = \nu C_d \left[1 - \exp(-\frac{t}{R_s C_d})\right] + (mt + b), \quad \text{(S2)}$$

which is the expression in equation S1 plus a linear component and a constant. The extra terms were added because the data in Fig. S10a do not exhibit saturation after the exponential rise, probably due to intercalation processes as discussed previously. The fitting results for $C_d$and R_s are plotted in Fig. S10b. Indeed, exfoliation does increase the double-layer capacitance, suggesting an increase in the surface area. Additionally, the solution resistance decreases for exfoliation up to 7 V and increases for exfoliation above 8 V, which corroborates the electrochemical impedance spectroscopy data discussed in the manuscript.

Note: we analyzed the data for 3.16 mV/s because these data complied well to equation S2. For faster scan rates, the charging/discharging processes would involve higher order effects and so could not be fully captured by the simplified expression in equation S2.

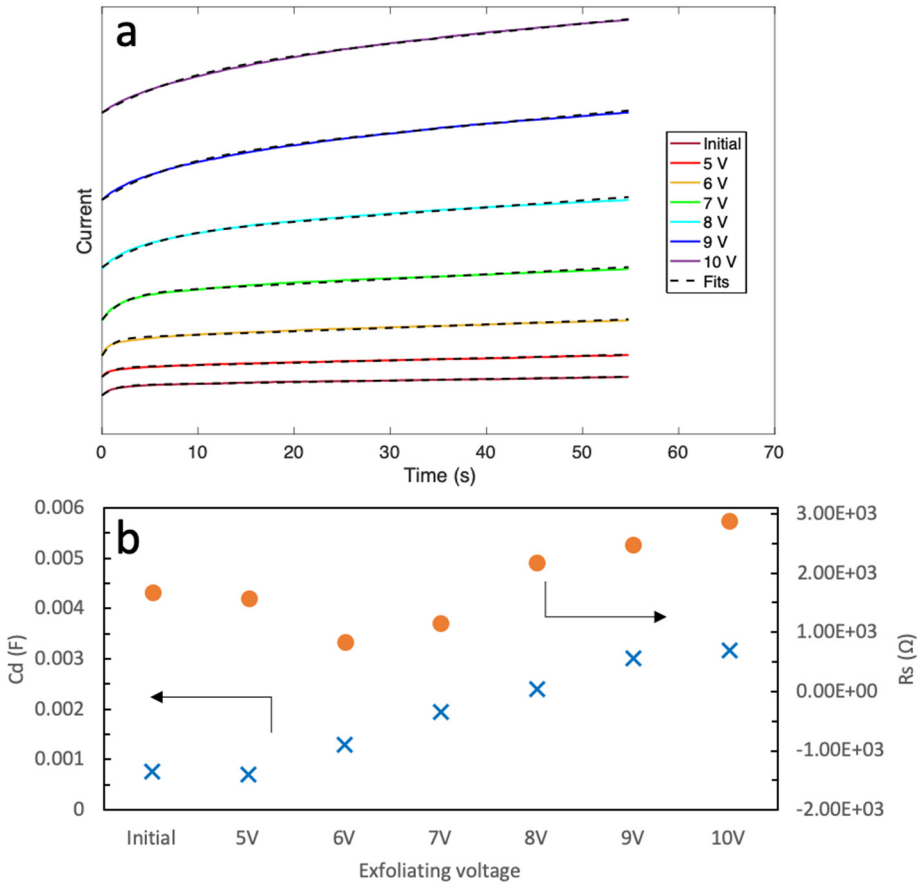

Figure S10. (a) Initial current response for each degree of exfoliation. Scan rate 3.16 mV/s. (b) Extrapolated double-layer capacitance and solution resistance for each degree of exfoliation.

References

(1) Winter, M.; Besenhard, J. O.; Spahr, M. E.; Novák, P. Insertion Electrode Materials for Rechargeable Lithium Batteries. *Adv. Mater.* **1999**, *10*, 725–763.

(2) Lian, P.; Zhu, X.; Liang, S.; Li, Z.; Yang, W.; Wang, H. Large reversible capacity of high quality graphene sheets as an anode material for lithium-ion batteries. *Electrochim. Acta* **2010**, *55*, 3909–3914.

(3) Yoo, E.; Kim, J.; Hosono, E.; Zhou, H.-s.; Kudo, T.; Honma, I. Large Reversible Li Storage of Graphene Nanosheet Families for Use in Rechargeable Lithium Ion Batteries. *Nano. Lett.* **2008**, *8*, 2277–2282.

(4) Bard, A. J.; Faulkner, L. R. Electrochemical Methods: Fundamentals and Applications, 2nd Ed.; Swain, E., Ed.; John Wiley & Sons, Inc.: New York, 2000; pg. 14–18.